[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hexamethylethane and Tetraalkylmethanes

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Because of the difficulty of preparing hexamethylethane and other tetraalkyl substituted methanes in quantity by following the methods given in the recent literature,[1] a practical method has been developed whereby a tertiary halide may be condensed with an alkylmagnesium halide giving yields of 11 to 20% of the desired hydrocarbon. This condensation has been brought about by the addition of cuprous iodide to a mixture of the straight chain Grignard reagent and a tertiary halide. This method also may be applied to the condensation of a branched chain Grignard reagent with a tertiary halide as shown in the case of hexamethylethane, obtaining a yield of better than 16% in a preparation of 1120 g.

Two series of hydrocarbons were prepared, the 2,2-dimethyl compounds from tertiary butyl chloride and RMgBr, and the 3,3-dimethyl compounds from tertiary amyl chloride and RMgBr. If the physical properties of each of these two series of hydrocarbons are arranged in order of increasing molecular weights, not only is there a regular increase in boiling points, but the refractive indices and densities exhibit the same regular increase in value for each series of similar hydrocarbons. The results obtained are summarized in Table I.

Experimental

As the preparations of the hydrocarbons were essentially the same, the details will be given only for 2,2-dimethylbutane and hexamethylethane. The remainder were made by the condensation of the suitable straight chain alkylmagnesium bromide with tertiary butyl chloride or tertiary amyl chloride in the presence of cuprous iodide. Their properties and yields from ten mole runs of Grignard reagents are given in the table.

TABLE I

	Yield, %	B. p. (760 mm.) °C.	n^{20}_D	d^{20}_4
2,2-Dimethylbutane	11	49.6	1.3709	0.6491
2,2-Dimethylpentane	21	79.0	1.3825	.6739
2,2-Dimethylhexane	14	106.2	1.3942	.6934
2,2-Dimethylheptane	17	130.4	1.4035	.7105
3,3-Dimethylpentane	22	86.0	1.3911	.6937
3,3-Dimethylhexane	17	112.0	1.4008	.7107
3,3-Dimethylheptane	16	137.2	1.4087	.7254
3,3-Dimethyloctane	11	161.2	1.4165	.7390

2,2-Dimethylbutane.—The Grignard reagent was made from 144 g. of magnesium with 1200 cc. of dry ether and 654 g. of ethyl bromide. The flask was cooled in ice and 400 g. of tertiary butyl chloride added with stirring. This was followed by 20 g. of cuprous iodide. The mixture stood overnight, during which time it solidified to a hard cake. This was decomposed by water and dilute acid. The ether extract was dried over solid potassium carbonate and fractionated. The crude hydrocarbon was shaken twice with cold concentrated sulfuric acid, followed by water, then sodium carbonate solution and finally dried over sodium sulfate. It was then refluxed for six hours with sodium–potassium alloy and again treated with sulfuric acid.

Hexamethylethane.—To 6 moles of tertiary butylmagnesium chloride in 2 liters of dry ether with rapid stirring was added a mixture of one-half mole of tertiary butyl iodide and five and one-half moles of tertiary butyl chloride. Much gas came off. Twenty grams of cuprous chloride was then added in 2-g. quantities. The reaction mixture heated up considerably, giving off gas and soon formed a hard cake. After standing overnight it was heated on a steam-bath until no more ether distilled. Dilute acid was then dropped slowly into the flask, the ether and hydrocarbon distilling off during decomposition. After the solid had dissolved, the residue was steam distilled. The hydrocarbons then were separated roughly by distillation, obtaining a product boiling at 104–106°. This crystallized in the receiver. This product was then crystallized from ether at −50° and redistilled from sodium taking a fraction boiling at 105–106° at 735 mm. This product although not of extreme purity melted above 99° and the crystals were dry; yield, 1120 g. from 60 moles of *t*-butylmagnesium chloride.

Summary

A practical method is given for the preparation of hexamethylethane and other hydrocarbons containing a tertiary group by condensation of an alkyl Grignard reagent with a tertiary halide by means of cuprous iodide.

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(1) Flood and Calingaert, THIS JOURNAL, **56**, 1211 (1934); Whitmore, Stehman and Herndon, *ibid.*, **55**, 3805 (1933); C. R. Noller, *ibid.*, **51**, 594 (1929).